KINETIC STUDY OF MONOSILANE PYROLYSIS FOR POLY-CRYSTALLINE SILICON PRODUCTION IN A FLUIDIZED BED

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Monosilane pyrolysis was conducted over the temperature range of a fluidized-bed reactor (823 K–973 K) by use of both packed-bed and tubular free-space reactors, with and without seed silicon particles, respectively. In the packed-bed reactor, the heterogeneous reaction was predominant and most of the silicon produced was deposited on the seed silicon surface. In the free-space reactor, the homogeneous reaction was predominant and fine powder was formed. The conversion of monosilane obtained was analyzed, based on the assumption of first-order reaction to silane concentration. The homogeneous reaction rate and heterogeneous reaction rate were separated and the rate constants of both reactions were determined. The activation energies were 231 kJ and 193 kJ respectively. The rate obtained was compared with the previously reported kinetics, obtained under different conditions from the present experimental conditions. In a reaction zone with a number of particles, such as the emulsion phase of a fluidized bed, the contribution of the homogeneous reaction was found to be less than 10% for the particles and temperature range employed in the present study.

Introduction

Lately, the demand for semiconductor-grade silicon has been increasing. The conventional Siemens process for production of polycrystalline silicon (poly-Si) from trichlorosilane has many problems. The problems of the filament process with rods in a bell jar reactor employed in the Siemens process are as follows: (1) low thermal efficiency and high electricity cost because of the external cooling required to prevent deposits on the reactor wall, (2) low throughput and (3) difficulties in continuous operation and scale-up. The Komatsu process is another commercial process for poly-Si production using a rod-type reactor. The process of production from monosilane, employed in the Komatsu process, has various merits over production from trichlorosilane: (1) higher yield of poly-Si from metallic silicon because of the absence of byproduct such as silicon tetrachloride, (2) higher one-pass conversion and no necessity of recycle of reactant, (3) absence of corrosive hydrogen chloride, (4) low cost for separation of impurities by distillation because of the low boiling point of monosilane, (5) higher purity of produced poly-Si and (6) lower deposition temperature⁷⁾.

The application of a fluidized-bed reactor to manufacture poly-Si from trichlorosilane has been

tried by NEDO (New Energy Development Organization, Japan)⁹⁾ and from monosilane by UCC/JPL (Union Carbide Corp.⁵⁾/Jet Propulsion Laboratory³⁾. These developments demonstrated the improvement of thermal efficiency by the application of a fluidized-bed reactor. However, many problems have been revealed: contamination from the reactor, deposition of silicon on the reactor surface and breakage of the fluidized bed, and clogging of particles in the bed.

In addition, entrainment of the fine powder formed by the gas-phase homogeneous reaction was also found to be a critical problem in the fluidized-bed CVD (chemical vapor deposition) process from monosilane. The fine powder, which readily adheres to the surface of the product, is easily contaminated in the course of its transportation and is difficult to handle in the later melting process.

Iya *et al.*⁶⁾ conducted an experimental study of the heterogeneous decomposition of monosilane in a fixed-bed reactor in the temperature range from 873 K to 1173 K. They found that powder formation was observed above a critical concentration, and the critical concentration was decreased by etching seed silicon and increasing reaction temperature. They also measured the heterogeneous decomposition rate at 849 K, 900 K and 949 K by use of a fixed-bed reactor. The measured rate was analyzed by assuming a

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first-order irreversible reaction and the reaction rate constant was written in the Arrhenius form. They concluded that a good operating point for the pyrolysis reactor is a silane feed concentration of 10% and a bed temperature in the vicinity of 913 K. Their measured rate is valuable, but the rate was the overall one and was affected by the specific surface area of seed silicon. Furthermore, the rate included the simultaneous homogeneous reaction rate. Therefore, special care may be needed to apply the rate to the analysis and design of a fluidized-bed reactor.

Hsu *et al.*⁴⁾ conducted fluidized-bed experiments and measured the elutriation of fines from the reactors. The measured percentage of fines elutriation was generally below 10% of the silicon-in-silane feed, and was much lower than the theoretical prediction calculated from the heterogeneous decomposition rate data by Iya *et al.*⁶⁾ and the homogeneous decomposition rate data by Hogness *et al.*²⁾ They concluded that the optimal operating temperature from the viewpoint of fines elutriation and deposition morphology is $T=973$ K. They also suggested that feed of high silane concentration ($> 50\%$) can be used without excessive fines generation within the vicinity of the optimal operating temperature. Though their conclusion is worth noting, the kinetic data presented by Hogness *et al.*²⁾ were obtained in the temperature range from 653 to 763 K. Therefore, the application of those data to the analysis may not be reasonable.

In the present study, monosilane pyrolysis is conducted over the temperature range of fluidized-bed reactors (mainly 823 K–973 K) by both packed-bed and free-space reactors, with and without seed silicon particles, respectively. The effects of the reaction conditions, including the pretreatment of the seed silicon on the degree of crystallization, and the qualities and morphology of products will be discussed in a separate paper⁸⁾. In the present paper, the results of the kinetic measurements are described.

1. Experimental

1.1 Materials

The seed silicon particles used in the packed-bed experiment were prepared in the following manner. Polycrystalline silicon particles (grade OPL-200, provided by Osaka Titanium Co., Ltd., Japan) were crushed and sieved to a size in the range of 0.177–0.840 mm, giving an average particle diameter of 0.378 mm. In some experimental runs for measurement of the reaction kinetics, particles with diameter in the narrower range of 0.500–0.590 mm were also employed. The effect on the kinetics of impurities on the surface of the seed silicon particles was investigated by the following two etching procedures, using particles of the latter size. One procedure was the same as Iya *et al.* adopted: the

Fig. 1. Experimental flowsheet

particles were washed first with hot (353 K) hydrochloric acid for 30 min, then etched with a mixture of acetic acid, nitric acid, and hydrofluoric acid in the ratio 2:3:2 for 1 min to obtain particles with an averaged diameter of 0.414 mm. By this procedure, a silicon layer with an average thickness of 0.063 mm was removed. The other procedure was that only hydrofluoric acid was used for 10 min after washing by hot hydrochloric acid, almost keeping the average diameter.

1.2 Packed-bed reactor

The experimental flowsheet is shown in Fig. 1. The flow rates of monosilane and argon (diluent gas) were measured and adjusted by mass flow controllers. The reactor was a vertical quartz tube with inner diameter 10 mm at upper and lower part, where a water-cooled gas feeder and a gas sampler were inserted from both top and bottom ends of the tube to the ends of the reaction zone and were tightly connected with the tube. The reaction zone between the two coolers was packed with the seed particles. The end of the gas feeder was placed in contact with the top surface of the packed seed silicon. The inner diameter of the reaction zone was reduced to 4 mm to reduce the monosilane conversion. The length of the reaction zone ranged from 5.8 cm to 8.5 cm. Monosilane diluted with argon was introduced from the water-cooled gas feeder and the pressure of inlet gas was measured by a pressure gauge located just above the feeder. The reaction zone was electrically heated by an external furnace, and the temperature of the external surface of the tube at the middle of the reaction zone was measured with a CA thermocouple and controlled. The reacted gas withdrawn through the water-cooled gas sampler was introduced directly to a TCD gas chromatograph mounted with a column of Porapak® T and the concentrations of produced hydrogen and unreacted silane were measured.

1.3 Procedures of packed-bed experiment

The weighed seed silicon was packed in the reaction zone of the weighed tube and the voidage in the packed bed, ϵ , was determined. The reaction zone was heated to the desired temperature at the desired flow rate of argon. The monosilane at desired flow rate, initially

flowing in the bypass line, was switched to the line to the reactor. The produced gas composition and the pressure in the inlet line were intermittently measured every three minutes.

About 20 minutes after the monosilane introduction, the produced gas composition attained the steady-state value. In several experimental runs, the gas flow rates of reactant and diluent and temperature were changed. The new steady-state gas composition was obtained five to ten minutes after the change of the operating condition. Reproducibility of the steady-state value was checked by choosing the same condition at both the beginning and the end of each run. Only the steady-state values were analyzed. After the experiment was terminated, the weight of the silicon deposit on the seed silicon, including the deposit on the reactor wall, was measured, and it was confirmed that the total deposit weight was equal to the weight of silicon in the reacted monosilane, within an error of $\pm 5\%$.

1.4 Free-space reactor experiment

Another series of experimental runs were conducted by a quartz tube reactor without any seed particles ("free-space reactor").

The reactor employed for the present experiment is shown in Fig. 2. Argon gas was separately introduced through the preheater part of the quartz tube with internal diameter of 10 mm, packed with quartz sand, into the reaction zone of the free-space quartz tube with internal diameter of 10 mm, then was mixed with monosilane gas introduced through the water-cooled gas feeder. The exit gas was externally cooled and directly introduced to the gas chromatograph through a filter to collect fine powder produced by the homogeneous reaction. The weight of the collected fine powder and the silicon deposit on the reactor wall was measured and it was confirmed that the sum was equal to the silicon in the reacted monosilane. However, the contribution of the homogeneous reaction could not be determined because some fraction of produced fine powder adhered to the reactor wall at the external cooler. About 30 minutes after monosilane introduction, the produced gas composition attained the steady-state value. In several runs, the gas flow rates of reactant and diluent, temperature and length of reaction zone were changed. The steady-state gas composition was obtained about five minutes after the condition was changed. Analysis was made only for the steady-state values. Reproducibility of the steady state value was checked as in the packed-bed experiment.

2. Results

Since only monosilane and hydrogen gases were detected in the exit gas, it was confirmed that the overall reaction is expressed as follows.

Fig. 2. Detail configuration of free-space reactor

Fig. 3. Temperature distribution in packed-bed reactor ($T=973\text{ K}$)

2.1 Packed-bed experiment

The value of X was determined by the following equation.

$$X = P_H / (P_S + P_H/2) \quad (2)$$

The flow rates of argon used were 4.8 and 9.7 cm^3/s and those of monosilane were 0.053 and 0.107 cm^3/s at 293 K. The inlet concentrations of monosilane were 1.1 and 2.2%. The reaction temperature in the packed bed was chosen from 823 K to 973 K. In the present experimental runs, the bed voidage, ϵ , ranged from 0.368 to 0.402. It was confirmed by inserting a thin thermocouple at the argon flow rate employed for the present experiments that the temperatures in the water-cooled gas feeder and the sampler were lower than 573 K and that the temperature of the main reaction zone was kept constant at a desired value. An example of the temperature distribution in the bed is shown in Fig. 3. However, in the vicinities of the feeder and the sampler the temperature was far below the desired value and silicon deposit was hardly found

on the seed particles. The temperature profile in these regions was hardly changed and the length of the region with flat profile of desired temperature was increased with increased length of the reaction zone, L . Therefore, the effective reaction length was evaluated as $L - L^*$ by compensating the end effect in the vicinities of the feeder and the sampler of the length, L^* . The residence time of gas in the effective reaction zone, τ , was evaluated as follows.

$$\tau = (L - L^*)/U \quad (3)$$

where

$$U = Q_{293}(T/293)(P_{atm}/P_{av})(4/\pi d_t^2)/\varepsilon \quad (4)$$

Under the present experimental conditions, the correction factor of pressure, P_{atm}/P_{av} , was larger than 0.75. By assuming that the pyrolysis rate is first order to the silane concentration, the following equation is obtained.

$$dX/d\tau = k_p(1 - X) \quad (5)$$

In Eq. (5), the error caused by the volume change by Eq. (1) was small because the monosilane concentration was small. The reaction rate constant, k_p , is expressed as follows.

$$k_p = k_v + k_s S/V \quad (6)$$

where

$$S/V = (6/d_p)(1 - \varepsilon)/\varepsilon + (4/d_t)/\varepsilon \quad (7)$$

The heterogeneous and homogeneous reactions were assumed to take place simultaneously and the heterogeneous reaction rate was assumed to be proportional to the surface area. It was also assumed that the heterogeneous reaction rate constants on the seed Si surface and on the reactor wall were of equal value. When the present kinetic data is applied to estimation of the CVD rate on Si seed, the error caused by the above assumption will be small, because the area of the latter reaction was only about 10% that of the former reaction. In the packed-bed reactor, the heterogeneous reaction was expected to predominate⁸⁾. Therefore, the value of $-(UV/S) \ln(1 - X)$ was plotted against the length of the reaction zone, L according to the following equation, derived from Eqs. (3), (5) and (6).

$$(UV/S) \ln(1 - X) = -k_s^*(L - L^*) \quad (8)$$

$$k_s^* = k_s + k_v V/s \quad (9)$$

The results are shown in Fig. 4. Under the present experimental conditions, no obvious difference in the data was observed between etched and unetched silicon. All data with different gas velocities and monosilane concentrations fell on a straight line for a given temperatures. All the lines for different

Fig. 4. First-order plot of monosilane pyrolysis on seed surface in packed-bed reactor

temperatures intersected the abscissa axis at 2.0 cm. Therefore, the end effect, L^* , was determined as 2.0 cm under the present experimental conditions. The apparent value of heterogeneous reaction rate constant, k_s^* , was given as the slope of the line for each reaction temperature.

2.2 Free-space reactor experiment

The heating length (4.4–10.0 cm), the flow rate of argon (4.4–17.8 cm³/s at 293 K) and that of monosilane (0.123–0.493 cm³/s at 293 K) were varied. Consequently, the inlet gas concentration of monosilane was varied from 1.3 to 5.3%. Equations (3)–(7) are also valid in the free-space reactor, while the voidage in the reactor, ε , is 1.0. In the present experiments, the pressure difference between gas inlet and exit was small and the pressure in the reaction zone was smaller than 1.1 P_{atm} . 30–65% of silicon produced by silane decomposition was caught as fine particles on the filter paper or on the wall of the tube from the reactor to the filter. The rest was weighed as the increase in reactor weight. From visual observation, a fairly large number of produced fine particles were found on the reactor wall at the external cooler. Therefore, most of the produced silicon was in the form of fine powder with a diameter of one μm or less⁸⁾, and it can be assumed that the homogeneous reaction predominates. Thus the value of $-U \cdot \ln(1 - X)$ was plotted against the heating length L according to the following equation, derived from Eqs. (3), (5) and (6).

$$U \cdot \ln(1 - X) = -k_v^*(L - L^*) \quad (10)$$

$$k_v^* = k_v + k_s S/V \quad (11)$$

The results are shown in Fig. 5. All data at different gas velocities and monosilane concentrations fell on a straight line under a given temperature. All the lines

Fig. 5. First-order plot of monosilane pyrolysis in free-space reactor

for different temperatures intersected the abscissa at 2.0 cm. Therefore, the end effect, L^* , was determined as 2.0 cm also for the present free-space experimental conditions. The apparent value of the homogeneous reaction rate constant, k_v^* , was given as the slope of the line for each reaction temperature.

2.3. Determination of heterogeneous and homogeneous reaction rate constant

In both series of experimental runs, both homogeneous and heterogeneous reactions took place. Therefore, the intrinsic reaction rate constants, k_v and k_s , were separately determined from Eqs. (9) and (11). The equations were solved algebraically, using the value of k_s^* obtained from the packed-bed experiments and that of k_v^* from the free-space experiments for each experimental temperature. In the packed-bed experiments, the value of V/S ranged from 0.0033 to 0.0051 and the value of 0.0042 was employed as the average. In the free-space reactor experiments the value of 0.25 was employed for V/S , taking into account only the reactor wall area as surface area, S . The contribution of the area of the produced fines to the reaction rate was found to be negligible under the present experimental conditions, because little effect of inlet silane concentration and total flow rate on the value of $U \cdot \ln(1-X)$ was observed.

2.4 Arrhenius plot

The values of k_s and k_v are plotted against the reciprocal of the reaction temperature in Fig. 6 (Arrhenius plot). The k_s was formulated as follows.

$$k_s = 2.65 \times 10^{10} \exp(-1.934 \times 10^5/RT) \quad (12)$$

Both the absolute value of k_s and the activation energy

Fig. 6. Arrhenius plots of heterogeneous and homogeneous decomposition rate constants

were a little larger than the values calculated from the data presented by Iya *et al.*⁶⁾ The value calculated from Farrow's data of the growth rate of silicon film at low pressure was larger than that from the present data, while the activation energy was lower.

The obtained k_v almost fell on the extrapolated line of the data presented by Newman¹⁰⁾, formulated as

$$k_v = 9.3 \times 10^{13} \exp(-2.315 \times 10^5/RT) \quad (13)$$

However, the value was a little smaller than the extrapolated line of the data presented by Hogness *et al.*²⁾ and those by Schmidt¹¹⁾, and much smaller than the decomposition rate of monosilane in the induction period^{11,12)}.

3. Discussion

The contribution of the homogeneous reaction in the packed-bed experiment was about 10% at 973 K and decreased with decreasing temperature. It was therefore estimated that the effect of the difference in average diameter of particles employed in the present study on the obtained value of k_s was less than 4%. On the other hand, the contribution of the heterogeneous reaction on the reactor wall in the free-space reactor experiment was less than 30% at 823 K and decreased with increasing temperature. Additionally, the reproducibility of the steady-state value between the beginning and the end of a run suggested that the effect of the difference in the surface of the reactor wall was small.

The specific surface area of fine powder is a function of inlet monosilane concentration, P_{SO} , conversion to

fine silicon particles, X_f , and particle diameter of the fines, d_p , as follows.

$$S/V = 6P_{s0}X_fM/(RTd_p d_s) \quad (14)$$

From the results of SEM analysis⁸⁾, the diameter of the produced fine particles was found to be smaller than 1 μm . Considering the agglomerates formation, the value of $1.0 \times 10^{-4} \text{ cm}$ is employed as d_p in the following evaluation. The value of S/V for the fine particles is calculated to be 0.12 cm^{-1} for $X_f = 1.0$, $P_{s0} = 1.37 \text{ kPa}$, $M = 28.1$, $T = 973 \text{ K}$, $d_s = 2.33 \times 10^3 \text{ kg/m}^3$. The value of S/V is 3% of the S/V for the wall (4 cm^{-1}) and the contribution of the reaction on the surface of the fine particles is evaluated to be less than 1% in the free-space reactor. Though the diameter of fine power may be smaller than 1 μm in the reaction zone, the conversion is smaller than 1.0. Therefore, the above evaluation will also be valid throughout the reactor. For much higher inlet silane concentrations than that of the present experiment, the contribution of the deposition on the surface of the fine particles may not be negligible.

In the present experiments, the reaction was conducted in argon diluent, but in a commercial plant the reaction should be conducted in hydrogen diluent because hydrogen is the by-product of the reaction and should be recycled. The results may be affected by the hydrogen concentration. Further investigation may be needed.

In the fluidized-bed CVD reactor, the heterogeneous reaction is expected to predominate in the emulsion phase, while the homogeneous reaction predominates in the bubble phase. The production rate of fine powder in the bed is to be estimated by a combination of the present kinetics and a fluidized-bed model including the volume fractions of both phases, gas residence time and solid fraction in both phases, and mass exchange between phases. The present kinetics is also expected to be useful in analyzing clogging phenomena.

Conclusion

Kinetics of monosilane pyrolysis was measured over the temperature range of a fluidized-bed reactor (mainly 823 K–973 K) by use of both packed-bed and free-space reactors, with and without seed silicon particles, respectively. The rate of monosilane pyrolysis was analyzed, based on the assumption of first-order reaction to monosilane concentration. The homogeneous and heterogeneous rate constants were evaluated independently and the activation energies were determined respectively as 231 and 193 kJ/mol. The contribution of the homogeneous reaction in the overall reaction was estimated to be at most 10% under the dense bed condition with the particles employed in the present study at the temperature of

fluidized-bed CVD of silicon.

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Nomenclature

d_p	= average particle diameter	[cm]
d_s	= solid density	[kg · m ⁻³]
d_t	= inner diameter of quartz-tube reactor	[cm]
k_p	= apparent first-order rate constant of overall monosilane pyrolysis	[s ⁻¹]
k_s	= first-order heterogeneous reaction rate constant	[cm/s]
k_s^*	= apparent first-order heterogeneous reaction rate constant in packed bed	[cm/s]
k_v	= first-order homogeneous reaction rate constant	[cm/s]
k_v^*	= apparent first-order homogeneous reaction rate constant in free-space reactor	[s ⁻¹]
L	= length of reaction zone	[cm]
L^*	= length of end effects	[cm]
M	= atomic weight of silicon	[—]
P_{atm}	= atmospheric pressure	[kPa]
P_{av}	= average of inlet and outlet pressures	[kPa]
P_H	= local hydrogen pressure	[kPa]
P_S	= local monosilane pressure	[kPa]
P_{s0}	= inlet monosilane pressure	[kPa]
Q_{293}	= inlet gas flow rate at 20°C	[cm ³ /s]
R	= gas constant	[J · mol ⁻¹ · K ⁻¹]
S	= particle, fine, wall or total surface area in reaction zone	[cm ²]
T	= temperature	[K]
t	= time	[s]
U	= interstitial gas velocity	[cm/s]
V	= total volume of voidage in reaction zone	[cm ³]
X	= monosilane conversion	[—]
X_f	= monosilane conversion to fine particles	[—]
ε	= voidage fraction	[—]
τ	= residence time	[s]

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